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Abstract

1440328 Hot dipping in Al-Zn bath BETHLEHEM STEEL CORP 21 Sept 1973 44436/73 Heading C7F A ferrous substrate is hot-dipped in an Al-Zn- Si bath, and subsequently cooled at a rate of at least 20 F/sec, the cooling being continued until such time that the residual heat in the substrate does not tend to remelt the coating. Ferrous sheet or strip 1 is cleaned, pre-heated to about 1200 F in furnace 10, heated at 800 -1200 F in a reducing atmosphere (e.g. H_2) in chamber 11, fed into a bath 13 of 25-70 wt. per cent Al, balance Zn where Si is present in an amount not less than 0À5 wt. per cent of the Al. The emergent strip is wiped by heated air or steam at 17, and cooled in chamber 19 by jets of air or water to give the desired cooling rate.

Description

(54) CORROSION RESISTANT ALUMINUM-ZINC COATING AND METHOD
OF MAKING
(71) We, BEIRLEHEM STEEL CORPORA-
TION, a corporation organised under the laws of the State of Delaware, United States of America, of 701 East Third Street, Bethle- hem, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement::
This invention relates generally to metalliccorosion-resistant coatings on ferrous articles, such as steel sheet, strip, wire, fasteners, structural shapes and otrhe steel products, and more particularly to the provision of highly corrosion-resistant aluminum-zinc coatings on such products.

Aluminum-zinc coatings for steel strip and other steel products and methods of providing such coatings have been described in
U.S. Patents 3,343,930 and 3,393,089 to
A. R. Borzillo et al. Such coatings consist of an intermetallic layer on the substrate with an aluminum-zinc overlay. While the aluminum-zinc coated products described in these patents are corrosion-resistant and exhibit in normal corrosive environments corrosion resistance very much greater than similar galvanized products, accelerated corrosion tests have indicated that some problems could ,after long periods, arise with such products in severely corrosive environments. Such environments may include seashore environments immediately adjacent to the ocean or severe industrial environments, particularly where the environment has generally acidified characteristics.

Under accelerated tests of corrosion in test environments simulating such severely corrosive

environments, it has been found that patches of the aluminum-zinc overlay of the coating may have a tendency to flake off. This flaking is of a different character from the mechanical flaking which is encountered in galvanized or aluminum coatings upon bending or flexing of the ferrous metal substrate. This well known mechanical flaking of galvanised and aluminum coatings has been found to be due generally to excessive growth of a brittle intermetallic layer formed between the ferrous substrate and the metallic overlay. Severe bending of such coatings cracks the thick intermetallic layer, and the cracks are then propagated, causing portions of the coating to flake off.

In aluminum-zinc coatings, on the other hand, in certain severe test environments the aluminum-zinc overlay of coating flakes off in patches without any bending. Microscopic studies have shown that the aluminum-zinc coating in these cases separates along the interface between the intermetallic layer and the aluminum-zinc overlay. This separation, which leaves the intermetallic layer still adhering to the ferrous base metal, appears to be independent of the thickness of the intermetallic layer and appears to be the result of corrosion. This flaking of aluminumzinc coatings is hereafter referred to as corrosion flaking. The exact cause of corrosion flaking has so far eluded lengthy and painstaking research. Its development has, however been traced by the present inventors, and treatment to prevent corrosion flaking has been devised.

The present inventors have been able to trace the development of corrosion flaking and the present invention may obviate its deleterious effects so as to provide a new and improved corrosion-resistant aluminumzinc coated product.

The aluminum-zinc overlay of the coating, being essentially a two phase system, solidifies in two phases having variable compositions. The aluminum, being the highest melting of the two metals, tends to solidify first, as a solid solution, essentially in the form of dendrites, so that an alloy high in aluminum is initially precipitated from the molten coating. As more and more of the aluminum-rich material is solidified out, the remaining molten coating metal becomes increasingly richer in the relatively lower melting zinc.

The last molten metal freezes out as interdendritic material and is quite high in zinc content. Microstructures as revealed by amyl nitric etching of cross sections of the coating perpendicular to the plane of the coating show these zinc-rich regions as dark areas between larger light areas consisting of various compositions of alpha-aluminum solid solutins.

Microscopic examination has indicated that the zinc-rich regions corrode at a faster rate than the general matrix of alpha-aluminum material. This results in a somewhat porous coating after an extended period in a corrosive environment. This porous costing, nonetheless, under ordinary circumstances remains highly corrosion-resistant and continues to sacrificially protect the substrate metal from attack in most corrosive environments.In highly corrosive environments, however, such as acidified sodium chloride test environments which simulate seashore and severe industrial environments, once the corrosive action has corroded out some of the zinc-rich regions extending from the surface of the coating to the underlying intermetallic layer, a coating not previously treated according to the present invention may rapidly flake off along the interface between the aluminum-zinc overlay and the underlying intermetallic layer. The corrosion is apparently very quickly propagated along this interface once the corrosive action reaches it from the exposed surface of the coating, and causes a rapid peeling away, flaking or exfoliation of the coating.

The present inventors have discovered that the propagation of corrosion along the interface between the intermetallic layer and the aluminum-zinc overlay can be prevented by rapidly cooling the coating during its solidification period at a rate equal to or exceeding a critical minimum rate. For aluminum-zinc coatings in the vicinity of 55%, by weight aluminum-which is the optimum coating composition having the general corrosion properties to protect steel- the critical minimum rate is approximately 20 F. per second. Cooling of the coating at a rate equal to or exceeding this minimum rate has been found to result in a coating in which there is little or no harmful propagation of corrosion along the interface between the aluminum-zinc overlay and the intermetallic layer.By so cooling, a coating is produced which is very resistant to corrosion flaking. The area of the interface surrounding the zinc-rich regions, and apparently extending across the entire interface, is stabilized by the accelerated cooling so that there is little or no harmful propagation of corrosion along the interface. A coating cooled at a rate less than the critical minimum rate of cooling, on the other hand, remains unstabilized in the interfacial region, so that the coating is very susceptible to corrosion flaking.

In the accompanying drawings:
Figure 1 is a view of a coating line for applying and treating the coating of the present invention.

Figure 2 is a drawing of a photomicrograph of an etched cross-section of a solidified aluminum-zinc coating on steel sheet.

Figure 3 is a drawing of a phptomicro- graph of a cross-section of aluminum-zinc coating similar to that shown in Figure 2, but having been exposed to a corrosive environment for a period.

Figure 4 is a drawing of a photomicrograph of a cross-section of an aluminum-zinc coating which has been treated by the method of the present invention and then exposed to a corrosive environment for a period.

Figure 5 is a graph illustrating various cooling rates and their effect with respect to corrosion flaking of an aluminum-zinc coating.

The preliminary coating of a ferrous base such as steel may be initially accomplished substantially by the hot dip coating practice shown and described in U.S. Patent 3,393,089 to Borzillo et al. This procedure results in the attainment of an aluminum-zinc coating 31, as shown in Figure 2, in which an aluminum-zinc overlay 33 comprises a matrix of alpha-aluminum 34 with included regions of dark-etching zinc-rich material 35. The overlay 33 is adjacent to an intermetallic layer 37 comprised of intermetallic compounds formed upon the ferrous base metal 39.

Referring to Figure 1, a strip 1 composed of 28 gage rimmed steel with a carbon content of 0.06 wt. %, a manganese content of 0.31 wt. %, and other elements customarily found in rimmed strip steel, is fed from a pay-off reel 2 to a cleaning tank 3 containing an aqueous solution 4 of any suitable standard alkaline cleaning solution for steel strip.

The cleaning solution is preferably maintained at a temperature of approximately 180-200 F. The cleaned strip is scrubbed at scrubbers 5, and rinsed in a tank 6 with rinse water 7. From the rinse tank 6, the strip is led through rubber squeegee rolls 8, over rolls 9 and downwardly through a heating furnace 10, there the strip is heated to a temperature of approximately 12000F.

or greater to anneal the strip. The furnace 10 may be heated by combustion of natural gas and air in a ratio of 1 to 8.

From the furnace 10, the strip passes about a guide roll 11 and through a holding chamber 12 where the strip is partially cooled to approximately 8000 F. to 12000F.

A reducing atmosphere of approximately 99% hydrogen is preferably maintained in the holding chamber 12 to protect the strip from oxidation prior to its entry into a coat ing pot 13. The strip 1 then passes through a molten metal bath composed primarily of molten aluminum and zinc contained in the coating pot 13. The strip 1 is guided through the molten bath 14 by sinker rolls 15 and 15'. The strip enters the coating bath at a temperature of approximately 800" to 12000
F. The bath is preferably maintained at approximatedly 1130"F. Upon leaving the bath, the strip is passed through a wiping means to establish a desired thickness of molten coating upon the strip. The usual commercial coating weight will be approximately one-half ounce to 1 ounce per square foot (two sides), i.e., .8 to 1.6 mils average coating thickness for each side.A suitable wiping means may be a pair of gas wiping elements 16 having gas orifices 17 designed to provide a blast of gas across the surface of the strip to wipe excess coating metal from the surface. The wiping gas, which may be air, steam or other suitable gas, is supplied from any suitable source, not shown, through conduits 18. The wiping gas is pre ferably heated so that it does not have an excessive cooling effect upon the coating as it is wiped. As an alternative, the coating may be wiped by a pair of conventional exit rolls.

After the strip passes through the gas wiping dies 16, it is immediately passed into an accelerated cooling chamber 19 where it is contacted by a jet or jets of a cooling gas or vapor such as air, fine water sprays or other suitable cooling media supplied at a rate effective to cool the coating upon the surface of the strip at a rate of at least 200F.

per second during the solidification period of the coating metal. In the particular cooling apparatus shown, jets of air are directed at the strip surface from headers 20. Accele- rated cooling of the coating through its solidification range could also be attained by the use of suitable oil or water quenches, particularly for products other than sheet and strip.

The flow of cooling medium such as air necessary to attain a cooling rate of at least 20 degrees per

second will depend upon the speed of the line, the gage of the base mate- rial, the amount of coating deposited upon the strip and other factors. A practical ap- proach in determining the flow of cooling medium necessary for proper cooling according to this invention is to measure the temperature of the strip as it passes into the cooling chamber 19 and at several points as it passes out of the cooling chamber 19, and then based upon these measurements and the speed of the strip one can easily calculate the cooling rate provided by any selected flow of cooling medium in the cooling chamber 19.

Since an aluminium zinc coating is essentially a two component system, its solidification temperature extends over a fairly broad range which will vary depending upon the relative percentages of aluminum and zinc in the molten metal. For a composition of 55 wt. % aluminum and 43.5 wt. % zinc with the remainder substantially silicon, the solidification temperature range under nonequilibrium cooling conditions extends from approximately 1085"F. to 700 F. as may be seen by consulting the currently accepted
Presnyakov phase diagram for aluminumzinc system. While a bath containing about 55 wt. % aluminum is the preferred composition, the bath may contain 25 to 70 wt. % aluminum, balance zinc, to which has been added silicon in an amount not less than .5 wt. % of the aluminum content.A preferred range is 40 to 60 wt. % aluminum, balance zinc.

As taught in Patent 3,393,089 to Borzillo et al., it is necessary in a hot dip aluminumzinc coating bath to include silicon equal to at least .5% of the aluminum content of the bath in order to prevent excessive growth of the intermetallic layer. The beneficial effects of silicon in preventing excessive growth of the intermetallic layer extend from .5% of the content of aluminum in the molten coating bath up to the solubility limit of silicon in the molten bath. While more silicon could be used, an additional amount has no practical effect. The solubility of silicon in an aluminum-zinc bath varies according to the relative percentages of the bath components and the temperature of the molten aluminumzinc system and thus cannot be readily defined.However, it is believed that on the average the solubility limit of silicon in most molten aluminum-zinc coating bath systems will be about 12% of the aluminum content of the bath.

It is important for the cooling rate of the coating to be at least 200F. per second throughout substantially the entire solidification range of the coating. It is important to sustain the cooling rate until the coating is entirely solidified, which is frequently beyond the point at which the coating, or at least the surface of the coating, has the appearance of being solidified. After the entire coating is solidified it is additionally important that sufficient cooling be continued so that residual heat from the ferrous base metal does not tend to reheat the coating again above the lower portion of the solidification range.The reheating effect of the base metal depends to a large extent upon its gage so that a heavy gage material may require considerable additional cooling beyond complete solidification to continue to extract heat from the coating and base metal. Accelerated cooling of the strip and its coating may be started before the solidification of the coating starts if desired, but is not usually necessary.

It is essential, however. to have accelerated cooling equal to, or in excess of, the critical minimum rate over the solidification range of the coating in order to prevent later corrosion flaking of the coating.

After the strip 1 leaves the accelerated cooling apparatus 19 it passes upwardly over a dancer roll 21 and then downwardly to a take-up reel 22 from where it may be later removed for storage, use or in some cases further treatment prior to use.

While the entire corrosion mechanism is not completely clear, it is known that corrosion begins within zinc-rich material in severely corrosive environments as shown in
Figures 3 and 4. Figures 3 and 4 are representation of photomicrographs of a coating susceptible, and one not susceptible, respectively, to corrosion flaking. In Figure 3 the corrosion taking place through the zinc-rich material can be seen as dark leached-out areas 40, and it will also be evident that corrosion has proceeded along the interface between the aluminum-zinc overlay 41 and the underlying intermetallic layer 43 upon the surface of the base metal substrate 45 sufficient to cause the overlay 41 to begin to flake off. The inventors refer to this condition and the coating which is susceptible to it as a susceptible or "unstabilized" coating.

In In Figure 4 there is shown an aluminumzinc coating similar to that shown in Figure 3 but which has been cooled during freezing at an accelerated rate, viz., at a rate of at least 20"F. per second, to stabilize the coating and render it nonsusceptible to flakingtype corrosion. In this Figure 4, it is evident that although considerable corrosion has occurred in the zinc-rich material, the corrosion has not progressed along the interface between the aluminum-zinc overlay 41 and the intermetallic layer 43. The inventors refer to a coating which exhibits this lack of susceptibility to interfacial corrosion as a

"stabilized" coating.It is evident that the treatment of the invention, i.e., the accelerated cooling, has somehow stabilized the portions of the interface adjacent to the zincrich regions and render the interface nonsusceptible to rapid propagation of corrosion.

A considerable volume of investigation has so far not revealed any detectable structural differences between the unstabilized and stabilized coatings although it is clear from the difference in corrodability of these variously cooled coatings that some important physical or chemical differences must be present. The important factor, however, is that the stabilized coating is not susceptible to corrosion along the interface and thus is not subject to corrosion flaking.

Testing for corrosion flaking and stabilization is accomplished as follows. A coated sample is initially leached for 5 minutes with concentrated nitric acid to partially dissolve the zinc-rich materials. The sample is then rinsed in 10% ammonium hydroxide and then rinsed in water and dried. The coated sample is then exposed in a salt spray cabinet to a fine spray of acidified (with acetic acid) five per cent sodium chloride at a pH of 3.0 and a temperature of 950F. for 45 minutes, followed by two hours of drying with compressed air at room temperatures and finally 3-1/4 hours holding time in the salt spray cabinet at a temperature of 950F. This exposure-drying cycle is repeated a number of times. A coating is considered to be stabilized which survives 100 cycles of the above test procedure without exhibiting corrosion flaking.Since no propagation of corrosion along the interface can occur even in an unstabilized sample until some of the zinc-rich regions are corroded, the initial leaching with nitric acid decreases the test time necessary. If desired, therefore, the leaching may be omitted if the number of cycles is restandardized. The above test is very suitable for testing commercial weight coatings for corrosion flaking.

Figure 5 shows cooling curves for samples of pregalvanized experimental panels dipped directly into a molten aluminum-zinc bath at 11300F. for 30 seconds and cooled at various rates and in various cooling media.

The molten bath was a commercial type aluminum-zinc bath containing 55 wt. % aluminum. The temperature of each sample was continuously measured at the surface of the sample during cooling. The area of horizontal cross hatching includes those cooling rates which the inventors discovered provided stabilized coatings, i.e., coatings not subject to corrosion flaking. The area of vertical cross hatching includes those cooling rates which the inventors discovered result in unstabilized coatings, i.e., coatings which are susceptible to corrosion flaking. The area of diagonal cross hatching, on the other hand, includes cooling rates which would be expected to result in occasional corrosion flaking.The upper limit of the horizontal cross hatched area is a curve in which cooling was accomplished at approximately 200 F. per second in the solidification range of the aluminum-zinc coating. Additional laboratory and production samples have been cooled at rates representative of those shown in Figure 5, and when subjected to the corrosion testing procedure outlined above, have conformed to the corrosion flaking characteristics indicated by the various cross hatch ings in Figure 5.

VVHAT WE CLAIM IS:-
1. A method of producing a metal product having a coating containing 25-70 weight percent aluminum and the balance substantially zinc on a ferrous base by hot-dipping in a bath consisting of aluminum, zinc and at least 0.5 weight percent silicon based on the aluminum content, and cooling the coated

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Claims

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product said cooling being carefully controlled during substantially the entire solidification of said coating to maintain a cooling rate of at least 200F. per second and continuing cooling so that residual heat from the ferrous base metal does not tend to reheat the coating above the lower limit of the solidification range.

2. A method according to claim 1, wherein the solidification temperature range under non-equilibrium cooling conditions extends from 1085OF. to 700OF.

3. A method according to claim 1 or 2 wherein the bath contains 40 to 60 weight percent aluminum.

4. A method of preparing an aluminumzinc coated product as claimed in claim 1 substantially as hereinbefore described.

5. An article when prepared by the method of any of claims 1 to 4.